# Investigation of spectral and electrical properties of solution processed PEDOT: PSS/reduced graphene oxide- carbon nanotubes hybrid composites

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# Layout

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- Characterization techniques
- Results & Discussions
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# Investigation of spectral and electrical properties of solution processed PEDOT: PSS/reduced graphene oxide- carbon nanotubes hybrid composites


## Abstract:

Hybrid composites have been prepared by solution method using various MWCNT concentration and keeping rGO content constant in host poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) . Structural and morphological characteristics of the prepared composite films have been characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Field emission Scanning Electron Microscopy (FESEM) and Raman Spectroscopy, UV-Visible (UV-VIs) spectroscopy and Fourier transform Infrared (FTIR) Spectroscopy. The enhanced electrical conductivity as a result of improved dispersion of MWCNTs and rGO has been observed without affecting the optical properties in the visible region. The observed improvement in electrical and retaining of optical properties can be attributed to synergistic effect of MWCNTs-rGO network in the composite. This result suggests that such hybrid composite materials could be used as transparent conductor applications in optoelectronic devices.

# Introduction

- Organic electronics has emerged a lot in the last two decades due to their low-cost fabrication, ease of processing, flexibility and tunabilities in their properties.
- In PEDOT:PSS, the conductivity of the polymer is due to –PEDOT unit and the polar part, i.e., –PSS unit that helps the polymer for dispersion in H2O.
- The low-temperature behavior and mechanical brittleness of ITO make it unsuitable for flexible device fabrication.
- Better physical properties of Carbon nanotube and graphene
  - high aspect ratio of the order of $10^8$,
  - electrical conductivity of $10^7$ to $10^8$ $Sm^{-1}$,
  - thermal conductivity of 3300 $WmK^{-1}$ ,
  - Young's modulus of 1060 GPa and
  - tensile strength of 200 GPa
- To minimize or prevent graphene sheets from stacking and to improve the physical properties, combination of graphene.

# Materials and methods

1. Graphene oxide was prepared adapting modified Hummers' method [31]. Graphite powder (1 g) and $NaNO_3$ (0.5 g) were collected in a beaker containing 25 ml of H2SO4 and stirred in an ice-cooled bath for 1 h. Then, 3 g of KMnO4 was slowly added to the above mixture and stirred for another 2 h. Cooling bath was then removed with continuous stirring. When it reached room temperature, 100 ml of distilled water was added. As soon as distilled is added, gas evolved and rise in the temperature to 90 $^oC$. After 15 min, 300 ml of distilled water was further added and stirred for another 1 h. The reaction process was completed by adding 10 ml of 30% $H_2O_2$ dropwise to the above dispersion. The above dispersion was transferred to a 1-L beaker and diluted using distilled water and washed in vacuum filter repeatedly until the pH of the dispersion becomes neutral. The filtered material was extracted from the membrane filter and dried at 100 $^oC$ to obtain graphene oxide (GO).
2. The graphene oxide was reduced by Hydrazine hydrate to remove the oxygen functional groups.
3. The MWCNTs was prepared by pyrolysis method.The as prepared MWCNTs were purified by air oxidation followed by acid treatment and then washing many times to get rid off the acid.

# Materials and methods

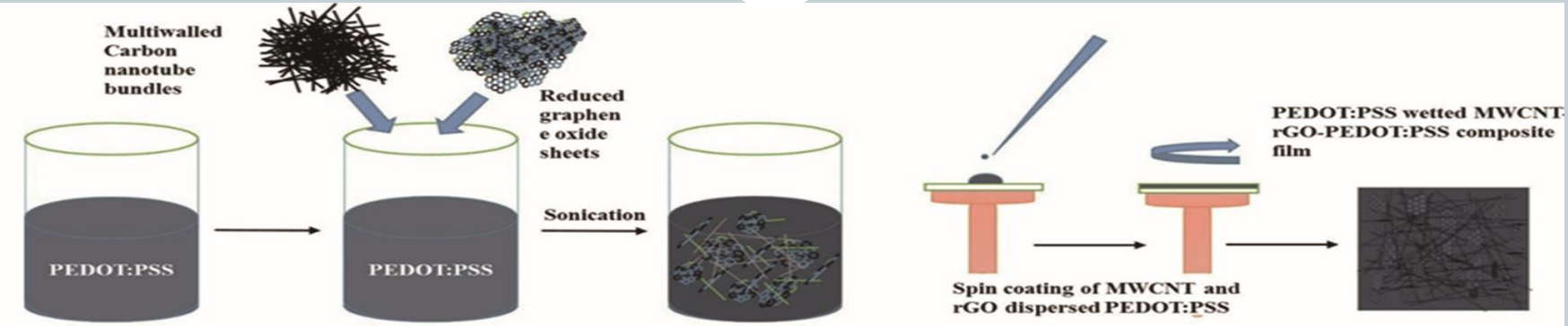



**Fig.1** Schematic diagram for fabrication of MWCNT-rGO-PEDOT:PSS composite films

- Keeping the quantity of rGO(1mg) and PEDOT:PSS(7ml) fixed in the dispersion, various wt% of MWCNTs were introduced and sonicated to prepare MWCNT-rGOPEDOT:PSS hybrid composites.
- The dispersion was sonicated for around 8 h when a deep blue-colored dispersion is obtained. For the deposition of the thin films, glass substrates were washed in detergent andrinsed in acetone and isopropanol for 10 min each.
- Spin coated at 1000 rpm for 1 min .

# Characterizations

- SEM characterization - Nova NanoSEM 450/FEI.
- X-ray diffraction measurement- (Ultima IV, Rigaku) equipped with a copper $K_\alpha$ source ($\lambda = 1.54$ A˚)
- FTIR spectra: perkin elmer spectrum 2
- UV-Vis spectra: perkin elmer lambda 850
- Raman spectra of PEDOT:PSS-based composites: Witech Raman Spectrometer
- Current–voltage by four probe contact method using a Keithley 2400 source meter.

# Results & Discussions

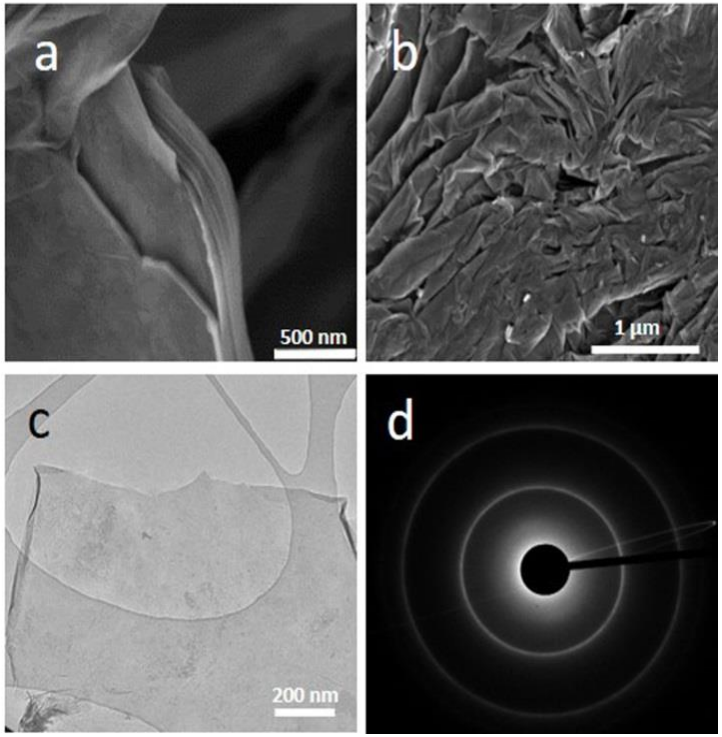



**Figure.1** SEM micrograph of (a) Graphite, (b) Graphene Oxide (GO), (c) TEM micrograph of GO (d) SAED pattern of GO showing the loss of crystallinity during oxidation process

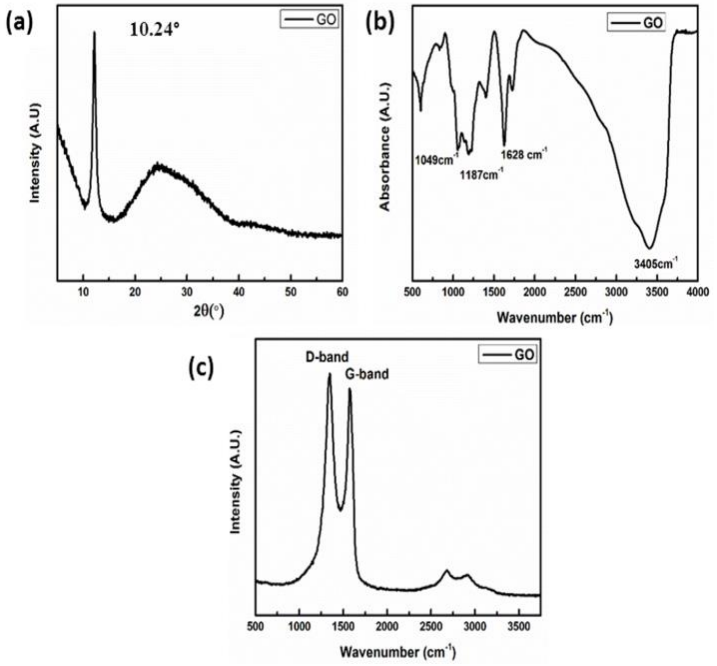



**Figure.2** (a) XRD, (b) FTIR and (c) Raman spectra of Graphene Oxide (GO)synthesized by modified Hummers' method

# Results & Discussions

## MWCNT and rGO

HRTEM image (Fig. 2c) reveals the well crystalized multiwalled nature of CNTs.

Diffraction peak at 26.4° - (002) planes which reveals the crystallinity as well as the graphitic nature of MWCNTs as well rGO

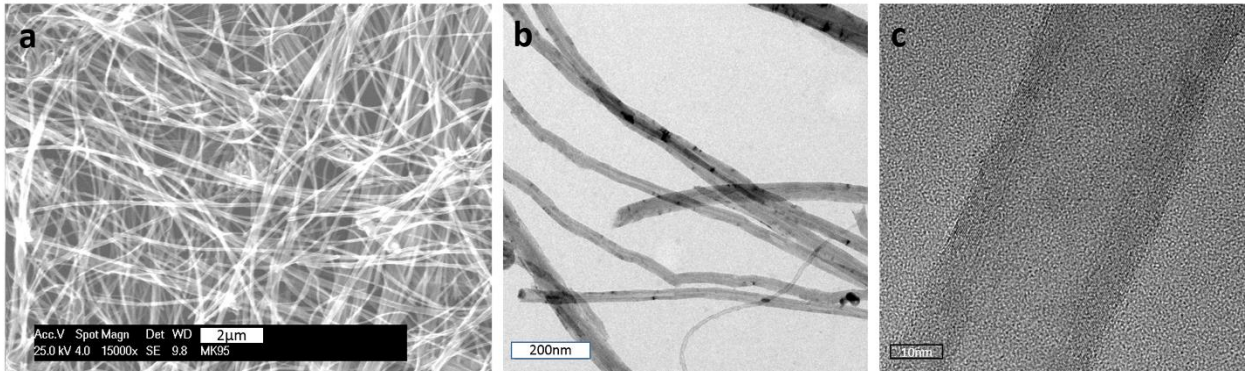
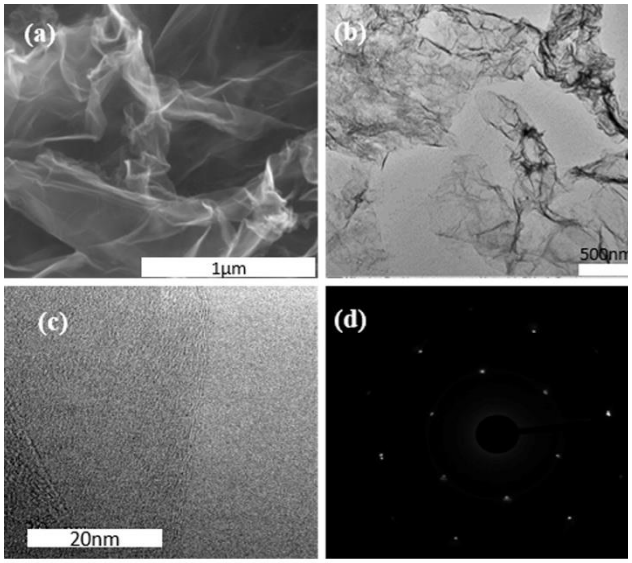



**Fig.2** (a) SEM Micrographs of purified MWCNT, (b) TEM of MWCNT (c) HRTEM of MWCNT showing the MWCNT nature of CNTs



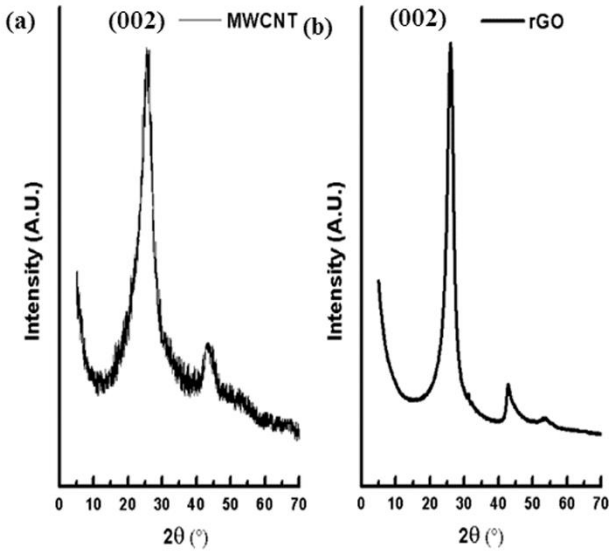




**Fig.3** (a) SEM (b) TEM (c) HRTEM and (d) of rGO

# Results, Cont.

**FTIR peaks (MWCNT)**

3539 and 2361 $cm^{-1}$ correspond to the –OH vibrations from carboxyl groups

1560 $cm^{-1}$ relate to the carboxyl ion stretching vibration

**FTIR peaks (rGO)**

1169 $cm^{-1}$ and 1049 $cm^{-1}$ corresponding to epoxy and carbonyl groups.

Peak at 1628 $cm^{-1}$- absorbed water molecules skeletal vibrations of un-oxidized graphitic domains

3449 $cm^{-1}$ and 2356 $cm^{-1}$ - remaining –OH groups and the adsorbed water

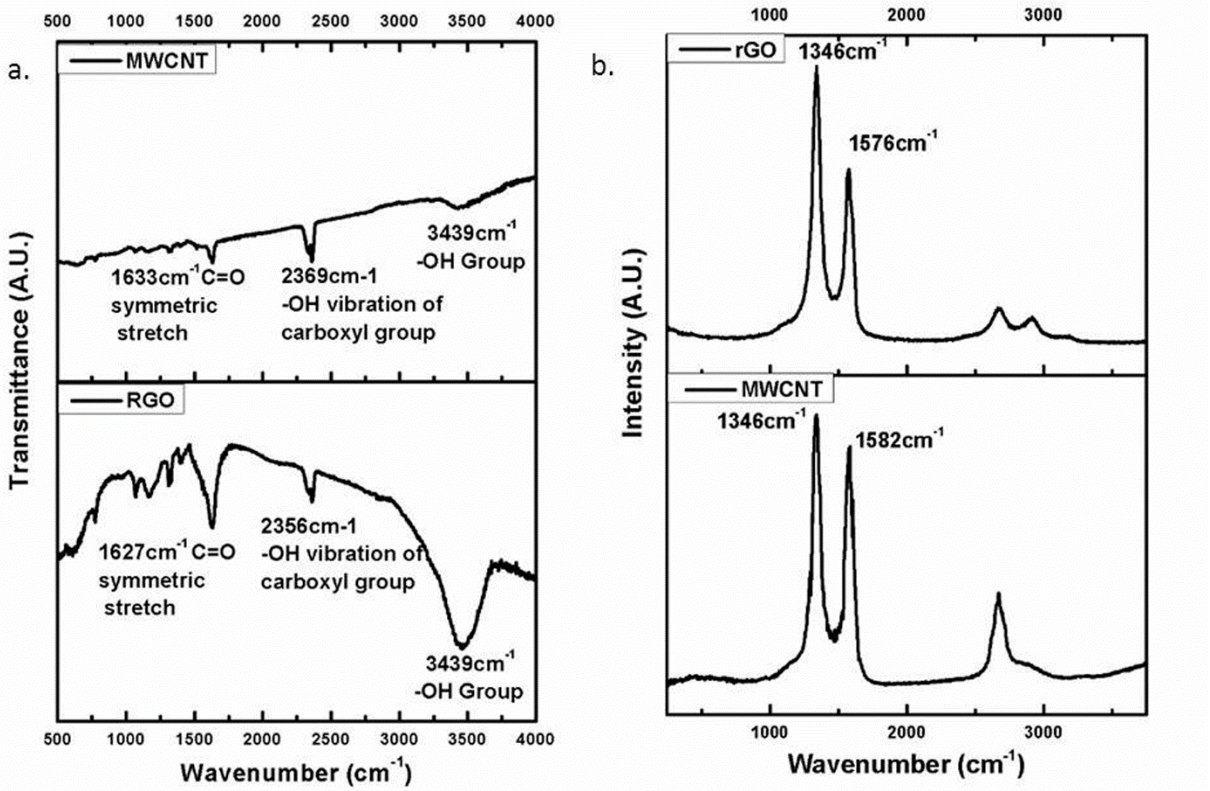



**Fig. 5** (a) FTIR of MWCNT, graphene oxide and reduced graphene oxide (b) Raman spectra of MWCNT, and reduced graphene oxide

Raman Spectra:
1346 and 1346 $cm^{-1}$ ---- disorder-induced D band
1582 and 1576 $cm^{-1}$ ----crystalline graphitic G band,

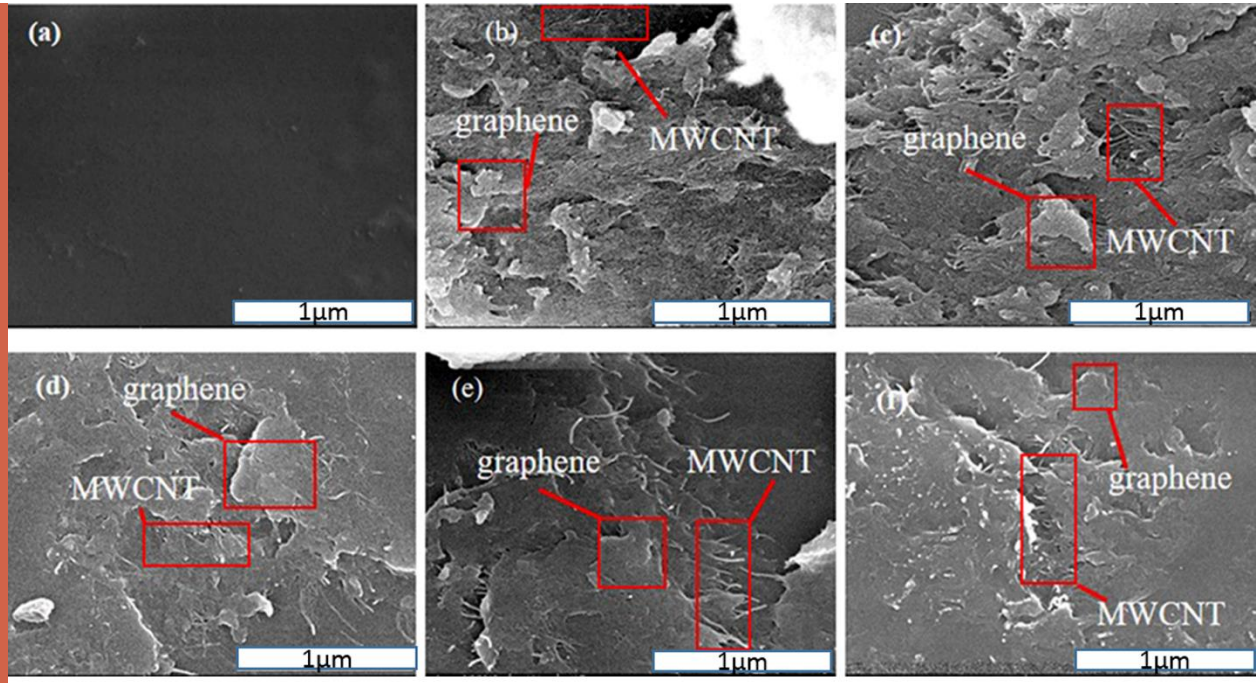
# Results Cont.

## SEM images

PEDOT:PSS-coated MWCNTs are encircled by blue ovals and the rGO sheets by the green circular shapes.

rGO and MWCNTs are well dispersed in the polymer matrix.

Better distribution of the graphene sheets is observed into the stacked structure of PEDOT:PSS (Fig. 6c) which is preventing agglomeration of CNTs in the composite.




SEM images of (a) pristine PEDOT: PSS film and (b - f) are MWCNT incorporated rGO-PEDOT: PSS hybrid nano-composites with 1.9wt%, 3.8wt%,5.6wt%, 7.3wt% and 9wt% MWCNT respectively

# Results Cont.

XRD peaks at 25.9° corresponds to (220) planes and 43.3° to that of (314) planes of tetragonal perovskite phase

FTIR

1525 and 1334 cm $^{-1}$ --- C=C and C–C stretching in the thiophene ring

840 and 937 cm$^{-1}$ ---- C–S bond stretching

1147 and 1056 cm $^{-1}$ --- ethylenedioxy group

1090 and 1206 cm$^{-1}$--- –SO2 and –SO3) sulphonic groups

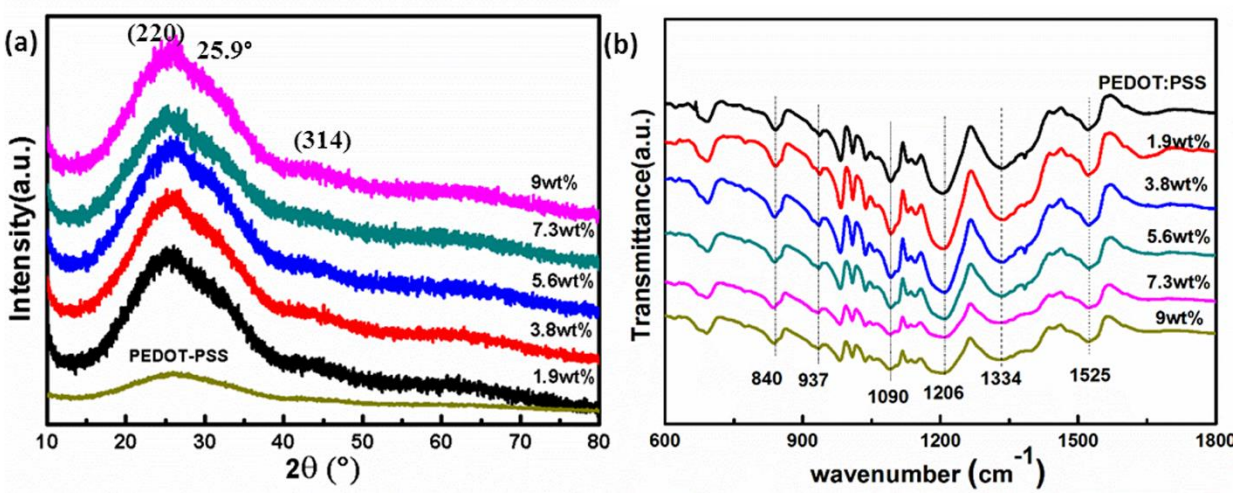



**Fig. 7** (a)XRD pattern and (b) FTIR spectra of MWCNT incorporated rGO-P3HT hybrid nanocomposites

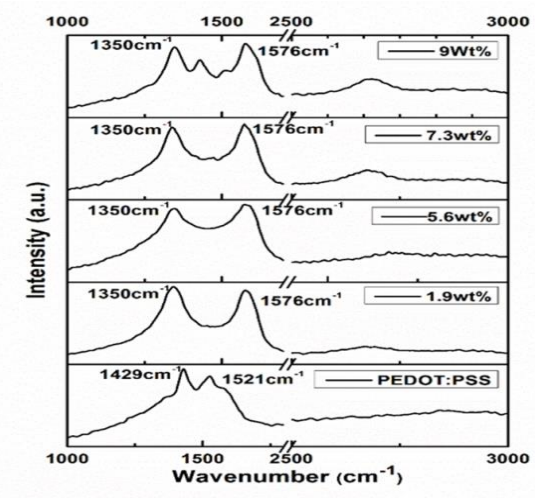



**Fig.8** Raman Spectra of PEDOT:PSS and MWCNT based composites in rGO/PEDOT: PSS host

**PEDOT:PSS**

1429 cm$^{-1}$ to the symmetric $C_\alpha$–$C_\beta$ Stretching peak at 1521 cm-$^1$---- asymmetric C=C structure and the symmetric $C_\alpha$–$C_\beta$ (–H) stretching of PEDOT:PSS

**MWCNT–rGO–PEDOT:PSS**

peaks 1429 and 1521 cm-$^1$ for PEDOT:PSS are suppressed in the composites due to convolution of the peaks at 1429 cm-1 with higher intense D band (350 cm$^{-1}$) and G band(1576 cm$^{-1}$ ) of MWCNT and rGO.

shift in D peak (1346 to 1350 cm $^{-1}$) suggests the structural changes

# Results Cont.

Absorbance peaks at 224 and 254 nm corresponding to the aromatic ring of – PSS group.

Absorbance of the composites in the visible region is barely affected by the addition of MWCNT and rGO

T= 10 exp(2-A)

Increase in conductivity with MWCNT wt%

Highest conductivity ( 3804 S/cm) observed for 7.3 wt% of MWCNT with a transparency of ~ 70%

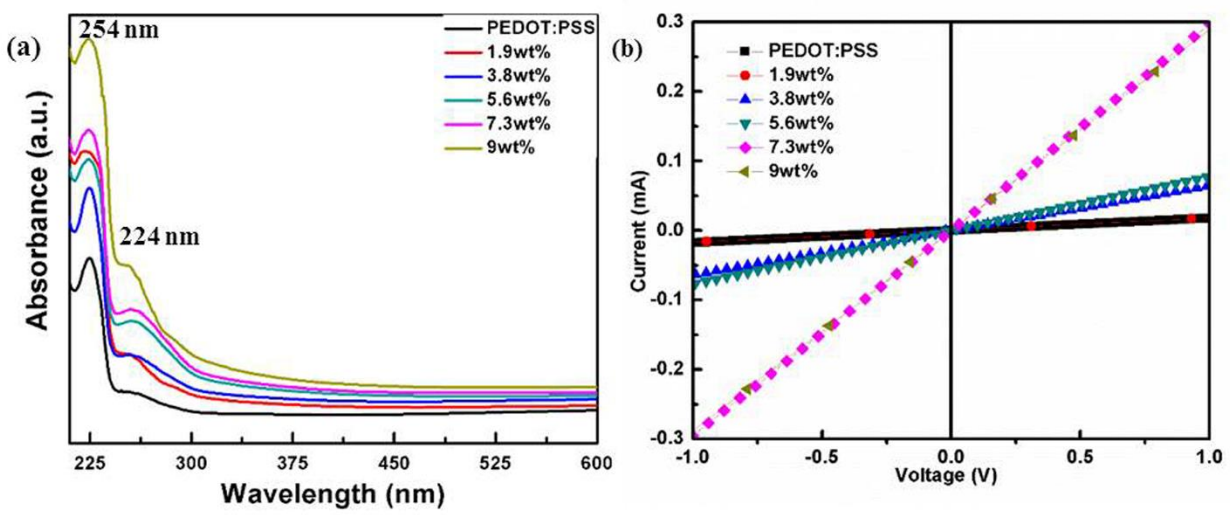



**Fig.9** (a) UV-Vis and (b) I-V characteristics of pristine PEDOT:PSS and MWCNT based composites in rGO/PEDOT: PSS host

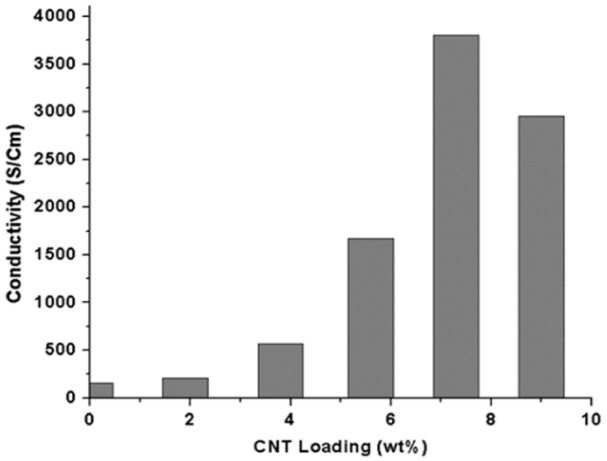



**Fig.10** Conductivity vs MWCNT loading in the composite

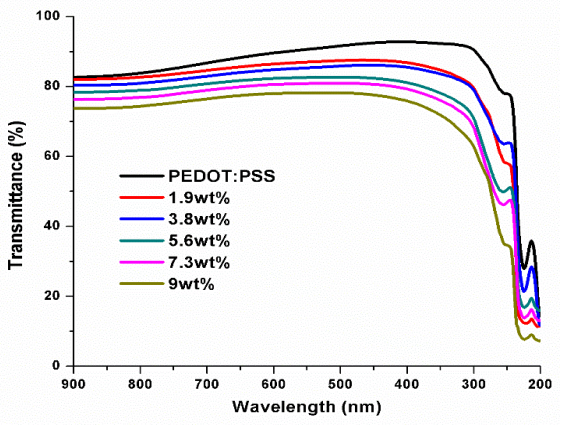



Fig.11 Transmittance of the composites obtained from the Absorbance

# Results Cont.

In the visible range (400-700nm) it could be observed that the absorbance is scarcely affected by MWCNT incorporation in the composite. The mild increase in absorbance due to MWCNT incorporation might be due to the blockage of some radiation by the filler network.

the transmittance in the UV-Vis_NIR region varies from ~83%- ~73% which reveals the probable application of the composite as transparent electrode in optoelectronic devices.

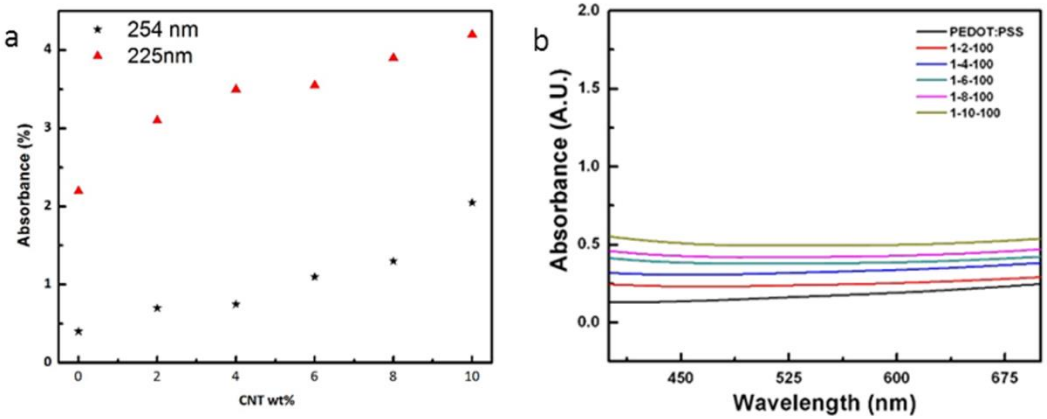



**Figure.4** (a) Absorbance corresponding to wavelengths 225nm and 254 nm and (b) UV-VIS absorbance spectra of MWCNT incorporated rGO-PEDOT: PSS hybrid nanocomposites with 1.9wt%, 3.8wt%,5.6wt%, 7.3wt% and 9wt% MWCNT respectively in the wavelengths at 400-700nm

# Conclusion

- Ternary composites comprising of MWCNTs, rGO and PEDOT:PSS have been successfully prepared by solution processing method.
- Hybrid nanocomposite films fabricated by spin coating method increase in electrical conductivities with MWCNT content. Maximum conductivity of 3804 S $cm^{-1}$ has been observed at 7 wt% of MWCNT which is comparable to that of indium tin oxide (conductivity 4000 S $cm^{-1}$).
- The observed optical properties of PEDOT:PSS-based hybrid nanocomposites in the visible range are barely affected by the incorporation of MWCNT and rGO into PEDOT:PSS.
- This increase in the electrical conductivity of hybrid polymer nanocomposites and unaltered optical properties is due to synergistic effect of 1D and 2D hybrid carbon nanostructures on the composite.

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Thank you